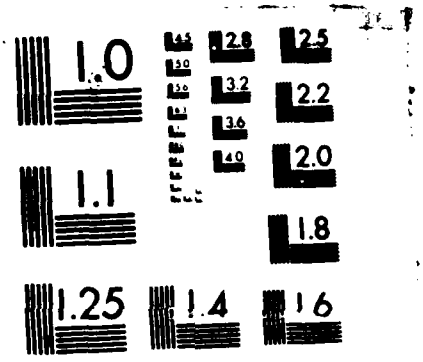
AD-A179 949 VIBRATIONAL DEACTIVATION AT SOLID SURFACES(U) CORNELL 1/1
UNIV ITHACA NY P L HOUSTON ET AL 12 MAR 87
ARO-20919 5-CH DAAG29-84-K-0016

UNCLASSIFIED F/G 20/5 NL




MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

DTIC FILE COPY

ARO 20919.5-CH

(2)

AD-A179 949

# Vibrational Deactivation at Solid Surfaces

**FINAL REPORT**

Paul L. Houston and Robert P. Merrill

January 1, 1984 through December 31, 1986

**U. S. Army Research Office**

**Grant Number: DAAG29-84-K-0016**

Cornell University

Ithaca, New York 14853

DTIC
ELECTE
MAY 05 1987
S D
D

Approved For Public Release;

Distribution Unlimited

87 4 30 205

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

A179979

# REPORT DOCUMENTATION PAGE

| | |
|---|---|
| 1a. REPORT SECURITY CLASSIFICATION: Unclassified | 1b. RESTRICTIVE MARKINGS |
| 2a. SECURITY CLASSIFICATION AUTHORITY | 3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited. |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) | 5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 20919.5-CH |
| 6a. NAME OF PERFORMING ORGANIZATION: Cornell University; 6b. OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office |
| 6c. ADDRESS (City, State, and ZIP Code): Ithaca, New York 14853-1301 | 7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211 |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office; 8b. OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-84-K-0016 |
| 8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211 | 10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO. |

11. TITLE (Include Security Classification): Vibrational Deactivation at Solid Surfaces

12. PERSONAL AUTHOR(S): Paul L. Houston and Robert P. Merrill

| 13a. TYPE OF REPORT | 13b. TIME COVERED | 14. DATE OF REPORT (Year, Month, Day) | 15. PAGE COUNT |
|---|---|---|---|
| Final | FROM 1/1/84 TO 12/31/86 | 1987, March 12 | 8 |

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

| 17. COSATI CODES | | |
|---|---|---|
| FIELD | GROUP | SUB-GROUP |
| | | |
| | | |

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Surface Chemistry, Energy Transfer, Vibrations, molecules

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The loss of vibrational energy was monitored by observing the decay of infrared fluorescence following pulsed excitation with a tunable infrared laser of molecules contained within a metallic or non-metallic cylindrical cell. The probability of collisional deactivation was obtained by measuring the decay time for the infrared fluorescence and dividing by the number of collisions per unit time calculated from gas-kinetic theory.

The exchange of translational and rotational energy was studied by scattering molecules from a well characterized single-crystal surface. A molecular beam was used to prepare the initial species in its lowest vibrational and rotational levels, while the scattered species were detected either in a state-selected measurement using laser-induced multiphoton ionization or in a total-flux measurement using electron impact mass spectrometry. (Keywords)

| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT | 21. ABSTRACT SECURITY CLASSIFICATION |
|---|---|
| ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS | Unclassified |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL | 22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL |

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

**FINAL REPORT**

# Vibrational Deactivation at Solid Surfaces

January 1, 1984 through December 31, 1986

Paul L. Houston and Robert P. Merrill

Cornell University

Ithaca, New York 14853

DTIC COPY INSPECTED 7

Accesion For

NTIS CRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification .....

By .....
Distribution /

Availability Codes

| Dist | Avail and / or Special |
|---|---|
| A-1 | |

**ARO Proposal Number: 20919-CH**

**Grant Number: DAAG29-84-K-0016**

## A. Statement of Problem Studied

This investigation focused on the exchange of translational, rotational and vibrational energy which takes place when a gas-phase molecule collides with a solid surface. Such processes are important to heterogeneous catalysis, corrosion, air filtration and pollution control.

The loss of vibrational energy was monitored by observing the decay of infrared fluorescence following pulsed excitation with a tunable infrared laser of molecules contained within a metallic or non-metallic cylindrical cell. The

probability of collisional deactivation was obtained by measuring the decay time for the infrared fluorescence and dividing by the number of collisions per unit time calculated from gas-kinetic theory.

The exchange of translational and rotational energy was studied by scattering molecules from a well characterized single-crystal surface. A molecular beam was used to prepare the initial species in its lowest vibrational and rotational levels, while the scattered species were detected either in a state-selected measurement using laser-induced multiphoton ionization or in a total-flux measurement using electron impact mass spectrometry. The angular intensity, rotational, vibrational, and velocity distributions of the scattered molecules could be determined as a function of crystal temperature.

## B. Summary of Results

**Surface Scattering:** An experimental system capable of measuring the rotational, vibrational, and translational state distributions of molecules scattered from surfaces was designed, constructed, and applied to the particular case of NO scattered from Ir(111). Rotational and vibrational state distributions were determined using multiphoton ionization spectroscopy (MPI). Translational state distributions were measured using time of flight (TOF) mass spectrometry, and angular intensity distributions were measured both selectively (using MPI) and non-selectively (using mass spectrometry). A computer-controlled pulse counting system was implemented to allow measurements to be made at extremely low molecular densities. Attempts were made to produce a beam containing vibrationally excited NO; a single mode F-center laser was used to excite NO ($v=2, J=3/2$) $\leftarrow$ NO ($v=0, J=1/2$) in a molecular beam with simultaneous

detection of the vibrationally excited NO via MPI. The theory and mathematical formalism of polarization spectroscopy was treated in detail.

Results from our laboratory on the interaction of NO(v=0,J) with Ir(111) have been published in a brief report; a more extensive report is in preparation. Briefly, the angular, velocity, and rotational energy distributions were measured. It was found that NO interacts strongly with the Ir(111) surface. In particular, for surface temperatures less than 300 K, where Ir(111) is covered by an overlayer of NO, a mixture of trapping-desorption and direct-inelastic scattering was observed. Our recent experiments have been directed toward elucidating the details of the NO/Ir(111) interaction that results in this mixture of scattering mechanisms. The velocity distributions have been investigated in more detail by varying beam energy, angle of incidence, and surface composition. For example, we have observed the expected shift of intensity in the trapping-desorption and direct-inelastic modes as the angle from the surface normal is increased or decreased from the angle of 48.5 ° used previously. As the angle of incidence increases, we observe a decrease in the fraction of translational energy lost to the surface. The velocity distributions were found to be insensitive to variations in surface coverage, including saturation of the surface with oxygen or N and O atoms. More recent efforts have been directed toward a more detailed understanding of the NO/Ir(111) surface chemistry. Sticking probabilities for NO as a function of surface temperature and beam energy have been measured in conjunction with temperature programmed desorption (TPD) profiles as a function of surface dosing temperature.

**Vibrational Deactivation:** The probability for deactivation for deactivation of CO(v=2) and $CO_2$(101) on collision with polycrystalline silver surfaces has been measured. The deactivation probability for CO(v=2) was found to decrease from 0.33 at 300 K to 0.20 at 440 K, while the deactivation probability for $CO_2$(101) was found to decrease from 0.72 at 300 K to 0.37 at 440 K. Since no population was observed in the CO(v=1) and $CO_2$(001) intermediate levels, it appears that each deactivation proceeds completely to produce the vibrational ground level. The magnitudes for the deactivation probabilities and the temperature dependencies indicate that a dominant mechanism for relaxation involves trapping and subsequent deactivation by one or more of several mechanisms, including electron-hole pair formation, vibration-to-rotation energy transfer, or perhaps even transfer of energy to the surface phonons. The experiments were performed in a UHV chamber by using a tunable infrared laser source to excite gas-phase molecules vibrationally before their collision with the surface and by measuring the population of vibrationally excited molecules through their time-resolved infrared fluorescence.

While this previous work in our laboratory has studied the vibrational deactivation of gas molecules at solid metallic surfaces, in an effort to learn more about the mechanism of vibrational deactivation, we have been extending our studies to non-metallic surfaces -- in particular, aluminum oxide and LiF.

Preliminary experiments on the deactivation of $CO_2$(101) at aluminum and aluminum oxide have been started. Aluminum is evaporated from a tungsten filament onto a cylindrical sample cell, in the same manner that silver surfaces were prepared in previous experiments. Aluminum oxide has been prepared by exposing the aluminum surface to 0.5 atm of pure oxygen for several

hours at about 200 °C. There are some difficulties associated with this experiment. One problem is that the sticking coefficient of $CO_2$ on alumina is not known. Infrared absorption studies[1] of $CO_2$ adsorbed on aluminum oxide indicate that the sticking coefficient is probably high, a result which will complicate the interpretation of any measurements we obtain. Another problem occurs with the difficulty in evaporating the aluminum. Although tungsten is typically the filament used in aluminum evaporations, it forms an alloy with aluminum, causing premature filament breakage. In order to make repeated measurements at various temperatures and pressures on freshly deposited aluminum surfaces, the filament must be replaced after only one or two evaporations, and the vacuum system must be baked after each replacement. This problem will lengthen considerably the time required to complete these experiments. Preliminary results on this system indicate that the vibrational deactivation probability is high for both aluminum and the oxide (about 0.6-0.7), but the results have not yet been reproduced enough to make comparisons between the two systems.

The experimental apparatus to be used for studying LiF is currently being designed. A rectangular, open-ended box has been constructed from four cleaved pieces of LiF single crystal, each approximately three inches long. The box will be placed inside a stainless steel block which will be used to heat the LiF evenly so that it can be cleaned. The block will be supported inside a specially built cell equipped with feed-throughs to be used for heating the block and for measuring the temperature. This cell will be put on the existing UHV chamber in place of the cylindrical cell that is being used for the

aluminum oxide experiments. LiF was chosen not only because it is a non-metal, but also because it can be cleaned and kept clean relatively easily.

## C. List of Publications and Technical Reports

1. J. Misewich, P. L. Houston, and R. P. Merrill, "Vibrational Relaxation of Carbon Dioxide (101) and Carbon Monoxide (v=2) During Gas-Surface Collisions," J. Chem. Phys. **82**, 1577-1584 (1985).

2. V. A. Apkarian, R. Hamers, P. L. Houston, J. Misewich, and R. P. Merrill, "Laser Studies of Vibrational Energy Exchange in Gas-Solid Collisions," Proceedings of the Seventeenth Jerusalem Symposium, Dynamics at Surfaces, 1984, D. Reidel, Dordrecht, Holland.

3. R. J. Hamers, P. L. Houston, and R. P. Merrill, "Direct-Inelastic and Trapping-Desorption Scattering of NO(v=0,J) from Ir(111): Angular, Velocity and Rotational Energy Distributions," J. Chem. Phys. **83**, 6045-6 (1985).

4. P. L. Houston and R. P. Merrill, "Vibrational Energy Exchange in Gas-Surface Interactions," Chem. Rev., submitted.

5. R. J. Hamers, P. L. Houston, and R. P. Merrill, "Competition between Direct-Inelastic and Trapping-Desorption in the Scattering of NO(v=0,J) from Ir(111)," prepared for submission to J. Chem. Phys.

6. R. J. Hamers, "Rotationally and translationally inelastic scattering of Nitric Oxide from Iridium(111), Ph.D. Thesis, Cornell University, 1986

7. J. A. Misewich, "Vibrational Deactivation during Gas-Surface Collisions," Ph.D. Thesis, Cornell University, 1984.

**D. List of Participating Scientific Personnel (with current addresses)**

Paul L. Houston
Department of Chemistry
Cornell University
Ithaca, NY 14853
(607) 255-4303

Dennis Masson
Graduate Field of Applied Physics
Cornell University
Ithaca, NY 14853
(607) 255-7195

Robert P. Merrill
School of Chemical Engineering
Cornell University
Ithaca, NY 14853
(607) 255-8656

Professor Ara Apkarian
Department of Chemistry
University of California
Irvine, CA 92664
(714) 856-6851

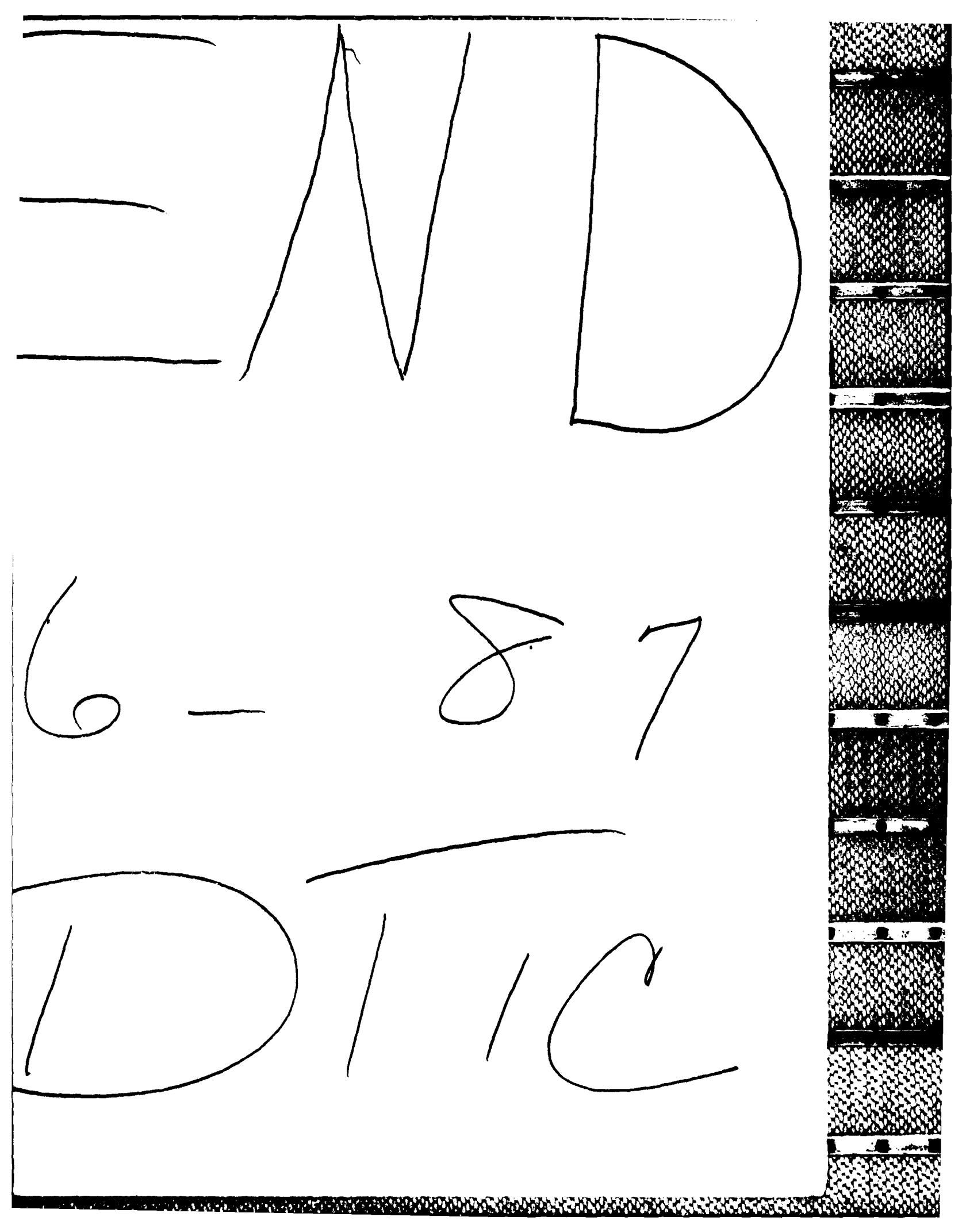
James Misewich (PhD 1984)
IBM
Thomas J. Watson Research
Center
Yorktown Heights, NY 10598
(914) 945-1620

Robert Hamers(PhD 1985)
IBM
Thomas J. Watson Research
Center
Yorktown Heights, NY 10598
(914) 945-1620

David Oakes (MS 1984)
Department of Chemistry
Cornell University
Ithaca, New York 14853
(607) 255-7195

Jeanne Sawicki (MS 1984)
Department of Chemistry
Cornell University
Ithaca, NY 14853
(607) 255-6419

H.-S. Shin
School of Chemical Engineering
Cornell University
Ithaca, NY 14853
(607) 255-7195)


END
6-87
DTIC